DOI 10.1007/s10717-014-9656-4
Glass and Ceramics, Vol. 71, Nos. 5 – 6, September, 2014 (Russian Original, Nos. 5 – 6, May – June, 2014)

COATINGS AND ENAMELS

UDC 666.293

SINGLE-FRIT NICKEL-FREE GLASS-ENAMEL COATINGS OBTAINED BY THE POESTA TECHNOLOGY

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Translated from *Steklo i Keramika*, No. 6, pp. 38 – 42, June, 2014.

The basic principles of the POESTA powder electrostatic technology used by enameling enterprises in Ukraine are examined and the requirements for powders and protective glass-enamel coatings are presented. The current problems arising in the synthesis of glass enamel for POESTA are analyzed. The results of investigations of the development and application of single-frit nickel-free glass-enamel coatings used for the purposes indicated are presented.

Key words: powder electrostatic technology, glass-enamel coating, synthesis, single-frit nickel-free compositions.

The advancement of the enameling industry is largely due to the development and adoption of fundamentally new enameling technologies. These include technologies for depositing coatings in an electric field: the electrostatic technology POESTA (Powder Electrostatic Application) and the slip electrostatic technology ESTA (Electrostatic Application) as well the electrophoretic technology ETE (Electrophoretic Enameling).

The POESTA technology has seen the most application. It is used in the production of enameled steel household appliances, hot water tanks, architectural and building elements, sanitary ware and elsewhere.

Even though POESTA was first used in the 1970s it has come into large-scale industrial use only in the last few years. This is due to the competition among producers of enameled products, a natural desire to improve quality and lower the productions costs. POESTA has made it possible to obtain glass-enamel coatings of exceptional quality while lowering energy consumption by 30 – 40%, reducing wastes to practically zero and eliminating a number of conventional operations, such as drying and surface preparation.

Today, large quantities of enameled household gas and electric plates, electric hot water tanks (EWH) with enameled interior tanks are produced in Ukraine by the POESTA technology. The bulk of these products are produced by the three largest enterprises: Greta JSC in Druzhkovka (Donetsk Oblast’), DZGiÉBA JSC (Nord PSC in Donetsk and UkrAtlantik JSC in Odessa). The main producer and supplier of glass-enamel frit and powders in Ukraine is Priméks TPK. The department of the technology of ceramics, refractories, glass and enamels at NTU KhPI is the principal developer of enamel compositions used in POESTA [1].

Fruitful collaboration between the producers of enameled products, frits and powders and the scientists united by the Ukrainian Association of Enamel Workers makes it possible to respond quickly to changes in the world market trends, the legal and standards base and the prices of raw materials and metals. In the present article we present the main advances in the development of new-generation compositions of glass-enamel frits and their adoption in electrostatic powder enameling of household appliances in Ukraine.

PRINCIPLES OF POWDER ELECTROSTATIC TECHNOLOGY POESTA

The electric field between a sprayer and a steel article is produced by the potential difference between a corona discharge on the spray gun and a grounded article. Free ions are formed as a result of the corona discharge and collide with

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neutral molecules of the air gases, resulting in the formation of new ions and electrons [2, 3]. The latter are accelerated in the electric field and also form ions in collisions.

Each electron forms along its path from the cathode to the anode a growing avalanche of charged particles. Positive ions, having acquired high energy, bombard the cathode (electrode of the spray gun) and knock new electrons out of it, thereby maintaining a strong current between the electrodes. The corona electrode is connected with the negative pole of the high voltage source (from 60 – 130 kV). A flux of negatively charged ions moves in the outer region of the corona discharge in the direction of the non-corona electrode.

The main condition for deposition of a high-quality coating on steel articles is that the glass-enamel particles must be able to acquire charge in the electric field of the corona discharge. The particles of enamel, which are dispersed in the air flow and acquire negative charge due to the presence of negative ions in the volume (a product of the corona discharge), are directed by the aerodynamic F_p and electric F_e forces toward the surface of the article (anode). These forces are countered by the resistance force F_s of the medium and gravity F_g. The electrostatic force F_e, acting in an electric field of intensity E on a charged particle with charge Q, equals $F_e = QE$ and is several-fold stronger than the force of gravity F_g acting on the same particle.

A charged particle of powder settled on the surface of a metal induces in the metal a charge of equal magnitude but opposite sign. If the conductivity of the particle settled on the metal article is high, the charge rapidly drains from the particle, after which the particle can be easily swept from the article by a stream of gas or can fall under gravity. Particles with low conductivity reside on the deposition electrode (article) for a longer time, which makes it possible for the second and third layers of powder to settle. Under the action of the electric field the second layer presses the first one to the deposition electrode, after which the particles in the first layer lose their charge. The electric field acts in precisely the same way on the charges of the particles in the third layer, settled on the second one, and so on. As a result of the constant pressure exerted by the newly settled particles of different size under the action of the gas stream the layer of enamel powder on the article forms a very compact, dense coating. The greater the resistance of the particles, the higher the density of the multilayer coating that forms in the process of deposition of the enamel powders.

The thickness uniformity of the deposited coating is a consequence of the self-smoothing of the layer due to the stronger attraction of the charged particles on thinner sections.

SPECIFICATIONS FOR THE POWDERS USED IN THE POESTA TECHNOLOGY

The POESTA technology requires special glass-enamel frit with a complex of properties that make it possible to deposit fine glass-enamel powders in a high-voltage field. The resistivity of the particles of enamel powder for deposition in a high-voltage electric field must be $\rho > 10^{11}\ \Omega \cdot m$ with granulometric composition in the range 3 – 100 μm, and the powder must possess the requisite flow properties. Such a resistance is secured by encapsulating the particles of enamel in hydrophobic substances. Encapsulation of the powder is accomplished by coating with organosilicon fluids during the milling process followed by solidification at temperature 150 – 200°C. A high degree of fluidization (fluidity) of the powder, equal to 90 – 150 g/30 sec, is attained in the process. The deposition of a hydrophobic sealant increases the electrical resistance of the fine glass-enamel powder on average by three to four orders of magnitude: from $10^7 – 10^8\ \Omega \cdot m$ of powder with no sealant to $10^{11} – 10^{13}\ \Omega \cdot m$ with a hydrophobic film. For this reason, in order to secure good adhesion (adhesion of powder to a steel base > 75%) the untreated glass powder must possess in a normal atmosphere the maximum possible intrinsic resistivity of at least $10^6 – 10^7\ \Omega \cdot m$ [5, 6].

These requirements, which are due to the particularities of the POESTA technology, are relevant for all types of glass-enamel powders irrespective of the type and function of the enameled articles.

BASIC REQUIREMENTS FOR PROTECTIVE GLASS-ENAMEL COATINGS

The operational characteristics of the glass-enamel coatings obtained are determined by the properties of the initial frit and must correspond to the specifications for a definite type of production (Table 1) [7].

The chemical stability of enamel coatings on the parts of household stoves under production conditions is determined by the 'spot' method — the action of a drop of 10% citric acid for 15 min. The chemical stability of glass-enamel coatings for interior tank water heaters is determined according to DIN 4753/3 (Table 1), using the procedure of DIN ISO 2744, by holding the samples in a 10% solution of citric acid or HCl for 1 h. The chemical stability class is evaluated on the basis of the exterior appearance of the samples after testing and their corresponding treatment following the international standards EN 14483-1-9, ISO 28706-2-2008 (Table 2). Testing to determine the luster by moving a lamp to a distance of 10 cm from an enameled surface is performed on samples with appreciable etching (classes C and D) [7, 8].

SYNTHESIS OF GLASS-ENAMELS FOR POESTA

Enamels for the POESTA technology are difficult to synthesize because the resistivity of the frits must be high while the coatings must have high chemical resistance and be relatively easy to fuse. In addition, at present frit developers and producers must work within the limitations on the choice of

TABLE 1. Requisite Properties of Coatings for Household Appliances

Stoves				Tank water heaters			
Property	Standard	Index	Remark	Property	Standard	Index	Remark
Chemical resistance	EN 14483-1-9; ISO 28706-2-2008	Class A	Spot test 10% solution of citric acid, 15 min	Chemical resistance	DIN 4753/3	min Class A	10% solution of HCl or citric acid, 1 h
Temperature stability of burner caps	ISO 4530	Undamaged coating	Heating to 400°C in 3 h	Water resistance	DIN 4753/3	Mass loss max 3.5 g/m^2	Boiling 504 h
Heat resistance:				Heat resistance	DIN 4753	Undamaged coating	3 tests 20 – 200 – 15°C (repeat 5 times)
– burner caps, grilles	EEA 8.6.4	Undamaged coating	20 – 380 – 15°C (repeat 5 times)				
– cooktops			20 – 200 – 15°C (repeat 5 times)				
– trays			20 – 260 – 15°C (repeat 5 times)				
Impact strength	ISO 4532	20 N	Damage diameter ≤ 2.0 mm after 24 h	Impact strength	DIN 4753; ISO 4532	10 N	Damage diameter ≤ 1.5 mm after 24 h
Bonding strength	EN 10209 Annex D	at least magnitude 3	Multilayer coatings – EEA 8.6.3	Physiological control	DIN 4753	Water extract from enamel should not contain lead or cadmium	
Coating thickness:				Coating thickness	DIN 4753	0.15 – 0.50 mm	
– burner caps and grilles	EN ISO 2178 2360 1463	min 0.15, max 0.60 mm					
– flat articles		min 0.15, max 0.40 mm					
Firing temperature		800 – 840°C		Firing temperature		840 – 860°C	

components for enamels, which is due to economics as well as the new sanitary-hygienic norms EC, specifically, the REACH 1907/2006 (annex v.11) instructions. These instructions stipulate nickel oxide content up to 0.1% in enamels. These limitations exclude from the frit composition for POESTA very important components, such as lithium, strontium and nickel oxides, and significantly reduce the content of TiO_2, P_2O_5 and conventional bonding activators, which also serve as colorants.

The laboratory of glass and enamels at NTU KhPI has worked out the scientific principles and criteria for synthesizing the compositions of glass-enamels for coating deposition by the powder electrostatic technology using different regimes for obtaining the powders: 2 layers/2 firings (2C/2F), 2 layers/1 firing (2C/1F) and 1 layer/1 firing (1C/1F) [9, 10]. Using these criteria we have developed and adopted in the production of electric and gas stoves easily fusible direct-on enamels with a complex bonding activator (CBA), making it possible to minimize the content of expensive components: cobalt, nickel and copper oxides. Owing to the optimized ratios of CoO, NiO, CuO, MnO_2 and Fe_2O_3 our CBA also gave the requisite color characteristics of the coatings obtained, specifically, black for the ovens of gas and electric stoves, corresponding to RAL 9004, 9005 [11].

The current requirements of the producers of enamel ware, specifically, household heating appliances, presuppose the use of a unified composition of glass powders for obtaining single-layer direct-on coatings and ground-coat coatings combined with covering coatings, in the 2C/2F and 2C/1F regimes.

It should be emphasized that the additional conditions for industrial adoption of these coatings included securing chemical stability no lower than class A even for articles which are not used in aggressive media (parts for household stoves). In addition, the particulars of production at the enterprises NORD PSC and Greta JSC limit the firing temperature of such chemically stable coatings to values no higher than 840°C. According to the classical principles of the theory

TABLE 2. Classification of Chemical Resistance of Glass-Enamel Coatings for Household Appliances

Chemical resistance class	External appearance of coating after test
AA	Coating with no changes
A	Possible dry abrasion
B	Possible wet abrasion
C	Image of lamp filament noticeable
D	Image of lamp filament not noticeable

a *b*

Fig. 1. Manifestation of antibacterial action of series Bn coatings: *a*) bactericidal action of B-3 coating against the bacteria *E. Cloacae* and *E. Coli*; *b*) growth of the bacteria *E. Cloacae* and *E. Coli* in a control medium.

and practice of enameling the chemical stability of A or higher class coatings is attained by means of the following technologies [8, 12, 13]:

– POESTA, by using high-silica refractory compositions for frits with firing temperature ≥ 860°C;

– slip technology, by milling refractory fillers SiO_2, ZrO_2, $ZrSiO_4$ and others;

– for both technologies, by a combination of several frits with different intervals of the fusibility and other physical-chemical properties.

In connection with the impossibility of using these methods for obtaining single-frit enamel for POESTA we advanced and experimentally implemented the following concept. The required properties of glass coatings can be attained by securing the structural strength of the glass matrix for particular temperature conditions by regulating the coordination state of the principal glass formers — boron and aluminum cations. We used these positions to synthesize universal coatings for articles in household stoves and single-frit nickel-free enamels for obtaining direct-on chemically and water resistant coatings on interior tank water heaters [14].

The current trend of securing antibacterial properties of coatings coming into contact with drinking water was taken into account in the development of glass-enamels for EWHs. Some types of microorganisms, such as *Enterobacter cloacae* and *Escherichia coli,* which form a biological film, owing to which they withstand ordinary disinfectants, develop on surfaces which are contact with water for a long time.

The antibacterial effect in glass-enamel coatings is due to either silver compounds or variable valence metal compounds specially introduced into them. Silver is the most effect and safe means, but the cost of the article increases considerably. For this reason we synthesized compositions of protective vitreous coatings whose antibacterial properties were due to bactericidal fillers containing ZnO, CuO, MnO_2 and CoO. These chemical substances act by oxidation of structural proteins and enzymes and therefore they are poisonous to the bacteria cells.

The antibacterial action of the series Bn glass-enamel coatings against the bacteria *E. Cloacae* and *E. Coli* (cultured in tap water with concentration 10^6 microbe cells in 1 ml) compared with a control sample was studied. Distinct bactericidal action was found: no growth of colonies of bacteria was found after thermostating for 24 h at 37°C (see Fig. 1) [1, 14].

CONCLUSIONS

The current specifications for the performance characteristics of enameled steel household appliances and heating units taking account of the international standards and economic trends as well as the new sanitary-hygienic norms EC have led to the development of universal coatings for protecting parts of gas and electric stoves and single-frit nickel-free enamels for obtaining chemically and water resistant antibacterial coatings by the POESTA technology for interior tank electric water heaters. The glass-enamel compositions developed at NTU NTU KhPI for powder electrostatic technology, characterized by electrostatic adhesion of powders for them ≥ 75%, a wide range of firing temperatures for the coatings (810 – 860°C) and class A chemical resistance (EN 14483-1-9, GOST 10798–85) have been adopted in the production of household stoves at the Greta JSC and the Donetsk Gas and Electric Household Appliances Works (Nord PSC). The single-frit nickel-free enamels for electric water heaters have been tested under laboratory conditions and are recommended for experimental-industrial testing.

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